



## HYDROLOGIC RESOURCE MONITORING PARAMETERS

# Groundwater Chemistry in the Unsaturated Zone



**Brief Description:** Water moves downwards through porous soils and sediments and, under favorable conditions, may preserve a record of weathering processes, climatic variations (in the Cl or isotopic signature), or human activities such as agriculture (NO<sub>3</sub>) and acidification (H<sup>+</sup>). This indicator may be considered as the output from the soil zone and may reflect the properties or change in properties of soils. Rates of downward movement are typically 0.1 to 1.0 m/yr, and a record of individual events (resolution 1-20+ years) may be preserved over a scale of decades or centuries [see groundwater quality; soil quality]. In contrast, records collected over periods of years are needed to establish trends from the monitoring of rivers and streams or groundwater discharge [see groundwater quality; surface water quality]. The unsaturated zone is also an important buffering zone for attenuation of acidity, metal content, and some other harmful substances.

**Significance:** Changes in recharge rates have a direct relationship to water resource availability. The unsaturated zone may store and transmit pollutants, the release of which may have a sudden adverse impact on groundwater quality.

**Environment where Applicable:** Temperate and semi-arid regions in particular. In temperate zones, the typical record may extend for 5-50 years, and in semi-arid regions 10-200 years.

**Types of Monitoring Sites:** Unconsolidated sediments or consolidated porous media (sand, till, sandstone, chalk, calcarenite, volcanic ash) on relatively level terrain (negligible surface runoff). The best records are obtained where the unsaturated zone is 10-30m thick, and where sediments and flow are relatively homogeneous.

**Method of Measurement:** Dry sampling of unsaturated zone sediments is carried out by hollow stem auger (hand or motor-operated), by sampling from dug wells, or by percussion or air-flush rotary drilling. Pore water is extracted from sediments by high-speed (13,000 rpm) centrifuge (drainage or immiscible liquid displacement) or, for non-reactive components such as Cl and NO<sub>3</sub>, by elution with de-ionized water. For isotopic samples (3H,  $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), vacuum distillation may be used. Measurement of Cl, NO<sub>3</sub>, SO<sub>4</sub> and other representative ions is made by standard methods suitably miniaturized to handle small quantities of water (eg. 5-10 ml).

**Frequency of Measurement:** 5-10 year intervals to confirm movement of solutes towards the water table.

**Limitations of Data and Monitoring:** Relatively homogeneous sediments are required where flow takes place uniformly ('piston displacement'). In dual porosity media, some by-pass flow may occur that needs to be taken into account, as when some contaminant travels relatively rapidly to the water table along fissures. In very dry sediments (<4% volumetric moisture content) it may be difficult to release pore waters, and elution must then be used.

Possible Thresholds: NA

### Key References:

Appelo, C.A.J. & D.Postma 1993. Geochemistry, groundwater and pollution. Rotterdam: Balkema

Cook, P.G., W.M.Edmunds & C.B.Gaye 1992. Estimating palaeorecharge and palaeoclimate from unsaturated zone profiles. Water Resources Research 28: 2721-31.

Edmunds, W.M. 1996. Indicators in the groundwater environment of rapid environmental change. In Berger, A.R. & W.J.Iams (eds). *Geoindicators: Assessing rapid environmental changes in earth systems*:121-136. Rotterdam: A.A. Balkema.

Geake, A.K. & S.S.D.Foster 1989. Sequential isotope and solute profiling in the unsaturated zone of British Chalk. *Hydrological Sciences Journal*, 34:79-95.

Edmunds, W.M., W.G.Darling & D.G.Kinniburgh 1988. Solute profile techniques for recharge estimation in semi-arid and arid terrain. In I. Simmers (Ed), *Estimation of Natural Groundwater Recharge*: 139-157. Higham, MA: Riedel.

**Related Environmental and Geological Issues:** Although inputs of pollutants can be monitored in the saturated aquifer, the resolution of data in the unsaturated zone is of high quality and unique value in providing an archive at annual or decadal scales.

**Overall Assessment:** Analysis of the chemistry of groundwater in the unsaturated zone is a technique of growing importance in groundwater quality assessment, and the only available fine-resolution means of gaining an instant record of long-term inputs to the hydrological cycle.

**Source:** This summary of monitoring parameters has been adapted from the Geoindicator Checklist developed by the International Union of Geological Sciences through its Commission on Geological Sciences for Environmental Planning. Geoindicators include 27 earth system processes and phenomena that are liable to change in less than a century in magnitude, direction, or rate to an extent that may be significant for environmental sustainability and ecological health. Geoindicators were developed as tools to assist in integrated assessments of natural environments and ecosystems, as well as for state-of-the-environment reporting. Some general references useful for many geoindicators are listed here:

Berger, A.R. & W.J.Iams (eds.) 1996. *Geoindicators: assessing rapid environmental change in earth systems*. Rotterdam: Balkema. The scientific and policy background to geoindicators, including the first formal publication of the geoindicator checklist.

Goudie, A. 1990. *Geomorphological techniques*. Second Edition. London: Allen & Unwin. A comprehensive review of techniques that have been employed in studies of drainage basins, rivers, hillslopes, glaciers and other landforms.

Gregory, K.J. & D.E.Walling (eds) 1987. *Human activity and environmental processes*. New York: John Wiley. Precipitation; hydrological, coastal and ocean processes; lacustrine systems; slopes and weathering; river channels; permafrost; land subsidence; soil profiles, erosion and conservation; impacts on vegetation and animals; desertification.

Nuhfer, E.B., R.J.Proctor & P.H.Moser 1993. *The citizens' guide to geologic hazards*. American Institute for Professional Geologists (7828 Vance Drive, Ste 103, Arvada CO 80003, USA). A very useful summary of a wide range of natural hazards.